Polymer Bulletin 27, 311–314 (1991)

Polymer Bulletin

Frequency-dependent activation energy of ac-conductivity in poly(4,4′-*N,N*-diiminosulphoxide diaminophenyl ether)

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SUMMARY

The ac conductivity of Poly(4,4'-N,N-diiminosulphoxide diaminophenyl ether) was measured at the temperature range 300-355 K as a function of frequency (range 10 Hz to 100 KHz). The activation energy at each frequency was calculated using the Arrhenius relation.

A mathematical formula was suggested to explain the dependence of the activation energy on the applied frequency.It was found that there is a good consistent between the experimental and the calculated value.

INTRODUCTION

The ac electrical conductivity (σ_{ac}) of conducting polymers has been the subject of intensive research work in recent years. Most of these studies were concentrated on the variation of σ_{ac} with the frequency and test temperature as well [1].

Polymers containing N-S links are very interesting due to superior electrical conduction [2,3]. Poly(4,4'-N,N-diiminosulphoxide diaminophenyl ether) is one of conducting polymers containing N-S links. This polymer has been recently prepared and its electrical conductivity had been reported [4]. It was found that the temperature dependence of σ_{ac} mostly shows a transition region around glass-transition temperature (T_g), which is of 355 K [4] .The change of σ_{ac} with temperature from room temperature up to T_g obeys the Arrhenius law in the form :

$$\sigma_{ac} \propto \exp(-Q/KT) \qquad (1)$$

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The value of **Q** was found to be frequency dependent, decreasing qualitatively with increasing frequency.

The aim of this article is to demonstrate the validity of this relationship for the studied polymer for temperatures below T_g .

EXPERIMENTAL RESULTS AND DISCUSSION

Poly(4,4'-N,N-diiminosulphoxide diaminophenyl ether) was prepared on reacting 4,4'-disulphinyl diphenyl ether by Micheal addition with 4,4'-diaminodiphenyl ether at 150 ^oC [4].

The frequency dependence of σ_{ac} at different temperatures was measured using a computer controlled lock-in technique. The measurements were carried out under vacuum ($\approx$10 Pa) at temperatures from 300 up to 355 K in steps of about 10 degrees and in the frequency range from 10 Hz to 100 KHz.

The activation energy **Q** was estimated for each frequency from the slope of (Ln σ_{ac}) vs (1/T) using the least square method. The variation of (**Q**) with the applied frequency **f** is represented in Fig.(1). It is clear from this figure that **Q** decreases continuously as **f** increases. It means that:

$$Q(f) = Q_o\,[1 - q(f)], \tag{2}$$

where Q_o is the dc activation energy, at $f = 0$, and **q(f)** is the energy decrement due to the increasing frequency. The function **q(f)** must satisfy the following limiting conditions:

$$q(f) = \begin{cases} 0 & \text{at } f = 0 \\ 1 & \text{at } f = \infty \end{cases} \tag{3}$$

A computer program was adapted to select the most suitable dependency from many formulas satisfying conditions (3) and giving best fit of the experimental data shown in Fig.(1). A relation of the form:

$$Q(f) = Q_o[1 - \exp(-f_o/f)]^{\alpha}, \tag{4}$$

was found to be the most probable function fitting satisfactory the experimental data of Fig.(1) with an error bar less than 10^{-4}. Taking the logarithm of eq.(4) we get:

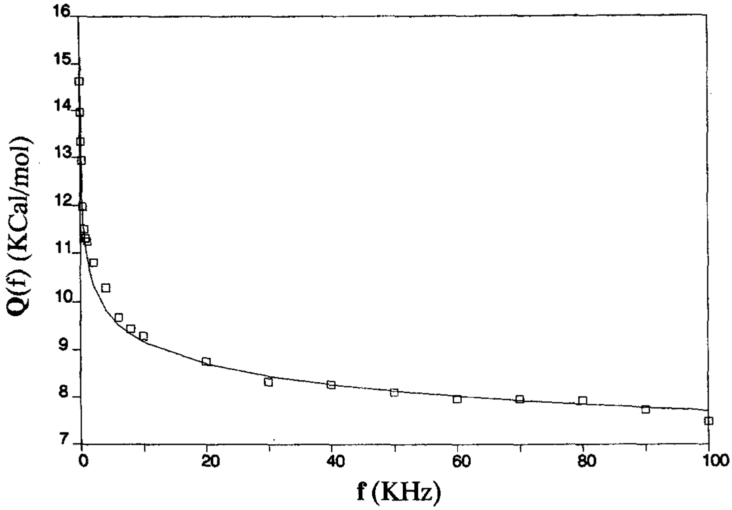

Fig.(1) The variation of the activation energy with the frequency.

$$\ln Q(f) = \ln Q_o + \alpha \ln [1-\exp(-f_o/f)] \qquad (5)$$

Equation (5) represents a straight line relation between **ln Q(f)** and **ln [1-exp(-f$_o$/f)]** of slope α and intercept **ln Q**. f_o is a constant having the dimension of sec $^{-1}$. Equation (5) is illustrated graphically in Fig.(2) for $f_o = 1$.

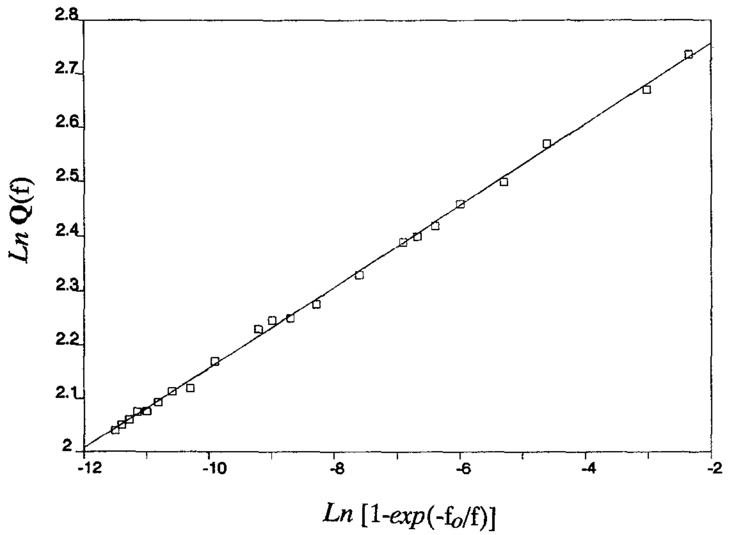

Fig.(2) Graphical representation of Eq.(5) using the experimental data of Fig.(1).

The LSM's results are $\alpha = 0.075 \pm 0.0002$, and $Q_o = 18.31 \pm 0.01$ KCal/mol.

On other hand, the dc electrical conductivity was measured for the same sample in the same temperature range mentioned before and in turn the dc-activation energy was obtained. A value 18.12 KCal/mol for Q_o was found. This excellent agreement between the two values of **Q** confirm the validity of the suggested formula.

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Accepted September 4, 1991 C